

# PATENT SPECIFICATION

DRAWINGS ATTACHED

967,261

Date of Application and filing Complete Specification: March 15, 1962.

No. 10011/62.

Application made in Germany (No. F33451 IVa/12g) on March 18, 1961.

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International Classification:—B 01 j (C 08 f)

## COMPLETE SPECIFICATION

### Reactor System

We, **FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT**, a joint stock company organised under the laws of Germany, of **Leverkusen-Bayerwerk**, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly the following state-

device and each of which is provided at the outlet with a lock comprising a chamber having an inlet and an outlet valve which valves are controlled by devices so as to effect the withdrawal of substances from the individual tube sections of the reactor system in a predetermined cyclic order or simultaneously at predetermined intervals. The ratio between chamber volume and tube volume is preferably

SPECIFICATION NO. 967,261

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:— Robert Schmitz-Josten, Gerstenkamp 9 Köln-Stammheim, Germany, Rudolf Haupt, Friedrich-Bayer-Strasse 9 Leverkusen-Bayerwerk, Germany, both German Citizens.

THE PATENT OFFICE.

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be kept constant within comparatively narrow limits for purpose of producing best possible products, and a strictly controlled residence time within the tube reactor is essential, the contents of each tube must remain constant during the reaction and a uniform withdrawal of product per tube must be ensured. With reactions under pressure, in which there is frequent withdrawal, the free cross-sections of the expansion valves are usually so small that a uniform withdrawal of the product is not guaranteed. Especially with the release of pressure of non-homogeneous reaction products or with gas-liquid mixtures, which separate into their components when the pressure is relieved, there is wear at the valves with frequent operation and this wear alters the cross-sections of the valves in a manner which cannot be controlled so that a uniform quantitative flow in the separate tube sections of the installation is no longer possible.

According to the invention there is provided a reactor system consisting of a number of tube sections which are connected in parallel to a common proportioning and mixing

differences occurring with the reaction thus obtained cause a periodic surging in the tubes and thereby a thorough mixing of the reactants even without using mechanical stirrer devices. Deposition of the reaction products on the walls of the tubes is prevented by the batch wise removal of said products, so that the danger of clogging is largely removed. The course of the reaction in the tubes can be very satisfactorily controlled. The arrangement according to the invention is capable of being used on installations of any desired size, only a single distributing arrangement being necessary for the supply of reactants to the many tubes. If a fault occurs in one tube section, this can easily be replaced without having to stop the entire installation.

The cyclic actuation of the driving means of the valves on the input and output sides of each chamber is preferably effected by a time relay or a contact manometer, which is set at the required working pressure.

The ratio between the chamber volume and the tube volume must be adjusted for each

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### Reactor System

We, **FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT**, a joint stock company organised under the laws of Germany, of **Leverkusen-Bayerwerk**, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a reactor system, for example for polymerization processes under pressure, the said reactor consisting of a plurality of tubular sections, which are connected in parallel to a common proportioning and mixing device and each of which is provided with a withdrawal device. Since it is necessary with many reactions, for example polymerization reactions, such as the copolymerization of ethylene and vinyl acetate, for the temperature in the reaction chamber to be kept constant within comparatively narrow limits for purpose of producing best possible products, and a strictly controlled residence time within the tube reactor is essential, the contents of each tube must remain constant during the reaction and a uniform withdrawal of product per tube must be ensured. With reactions under pressure, in which there is frequent withdrawal, the free cross-sections of the expansion valves are usually so small that a uniform withdrawal of the product is not guaranteed. Especially with the release of pressure of non-homogeneous reaction products or with gas-liquid mixtures, which separate into their components when the pressure is relieved, there is wear at the valves with frequent operation and this wear alters the cross-sections of the valves in a manner which cannot be controlled so that a uniform quantitative flow in the separate tube sections of the installation is no longer possible.

According to the invention there is provided a reactor system consisting of a number of tube sections which are connected in parallel to a common proportioning and mixing

device and each of which is provided at the outlet with a lock comprising a chamber having an inlet and an outlet valve which valves are controlled by devices so as to effect the withdrawal of substances from the individual tube sections of the reactor system in a predetermined cyclic order or simultaneously at predetermined intervals. The ratio between chamber volume and tube volume is preferably the same for the chambers of all tube sections. By means of this lock arrangement, an exactly proportioned quantity can always be withdrawn intermittently and at the correct time from each tube section and be expanded to a pressure below the reaction pressure, so that a uniform supply to the individual tubes from the common charging and distributing device is ensured. This arrangement guarantees an equal residence time, a uniform degree of reaction and an identical quality of product for all tubes. The pressure differences occurring with the cyclic expansion thus obtained cause a periodic surging in the tubes and thereby a thorough mixing of the reactants even without using mechanical stirrer devices. Deposition of the reaction products on the walls of the tubes is prevented by the batch wise removal of said products, so that the danger of clogging is largely removed. The course of the reaction in the tubes can be very satisfactorily controlled. The arrangement according to the invention is capable of being used on installations of any desired size, only a single distributing arrangement being necessary for the supply of reactants to the many tubes. If a fault occurs in one tube section, this can easily be replaced without having to stop the entire installation.

The cyclic actuation of the driving means of the valves on the input and output sides of each chamber is preferably effected by a time relay or a contact manometer, which is set at the required working pressure.

The ratio between the chamber volume and the tube volume must be adjusted for each

reaction so as to produce optimum results. This ratio depends on the residence time, the degree of conversion, the physical state of the reaction components and also on the mean reaction pressure. Since pressure differences are set up in the reaction tubes by the intermittent and cyclic withdrawal, an upper limit is set for the ratio between chamber volume and tube volume by the pressure fluctuation in the tubes which occurs with the filling and emptying of the discharge volume, if it is necessary not to fall below a certain minimum pressure or exceed a certain maximum pressure. Generally speaking, the ratio between chamber volume and tube volume will have a value of 0.0005 to 0.1. When reactions are carried out under pressure, a ratio of 0.002 to 0.1 has for example proved satisfactory. Since a storage vessel is arranged upstream of the tube sections as a proportioning device, the extent of the pressure fluctuations in the tubes can also be reduced by using a storage vessel of a suitably small size or by using a pressure in the storage vessel which is in excess of the maximum reaction pressure in the tubes.

Embodiments of the invention are illustrated in the accompanying drawings in which:—

Figure 1 shows diagrammatically one constructional form of a tube reactor, in which withdrawal from the individual chambers take place in a predetermined cyclic order as a function of time;

Figure 2 shows a construction of a tube reactor in which withdrawal from the individual tubes takes place simultaneously at predetermined intervals, and

Figure 3 shows a construction of a reactor system of tube sections which are provided with stirrers.

In the form shown in figure 1, gaseous reactants are introduced through the pipe 1 by means of the compressor 2 and through a pipe 3 into the mixing and storage vessel 4. Liquid reactants are supplied to the mixing vessel 4 from the pipe 5 by means of the pump 6 and through the pipe 7. The components are intimately mixed in the vessel 4, if necessary by the stirrer-device 8.

The reaction mixture flows from the storage and mixing vessel 4 through the distributor pipe 9 into the individual pipes 10, 10<sub>1</sub>, 10<sub>2</sub>, 10<sub>3</sub> to 10<sub>n</sub> and to the reaction tubes 11, 11<sub>1</sub>, 11<sub>2</sub>, 11<sub>3</sub> to 11<sub>n</sub>. The reaction is initiated and carried out in these reaction tubes by suitable temperature control. The tubes 11 to 11<sub>n</sub> are preferably all the same length and volume. Withdrawal chambers 12, 12<sub>1</sub>, 12<sub>2</sub>, 12<sub>3</sub> to 12<sub>n</sub>, are connected to the outlet ends of the tubes 11 to 11<sub>n</sub>, and the said chambers have controllable valves 13, 13<sub>1</sub>, 13<sub>2</sub>, 13<sub>3</sub> to 13<sub>n</sub> on the input sides thereof and controllable valves, 14, 14<sub>1</sub>, 14<sub>2</sub>, 14<sub>3</sub> to 14<sub>n</sub> on the output sides

thereof. The products removed from the reactor are discharged by way of the pipe 15 to a working-up installation. Cyclic withdrawal of the substances at the individual locks is effected as follows, taking the lock 12—14 as an example:

Phase 1: Opening of the valve 13 and filling of the chamber 12.

Phase 2: Closing of the valve 13 and a calculated safety interval beyond the closing time.

Phase 3: Opening of the valve 14 and emptying of the chamber 12.

Phase 4: Closing of the valve 14 and calculated safety interval beyond the closing time.

The phases 1 to 4 take place in each tube in turn with a constant time interval for each phase. The regulation of the pressure in the installation is achieved through the interval between successive openings of the valves 13—13<sub>n</sub> on the input sides of the respective chambers for example by a time relay.

The pressure regulation for the reactor system shown in figure 1 operates as follows:

The pressure of the tube system is measured through a measuring device 17. The measured value thereof is supplied to the input of a regulator 18, which has a PI-behaviour (proportional and reset control action). The regulator 18 influences the speed of a step-by-step switch 21, for example through the setting motor 19 of a regulating gear 20. A cam switch 22 to 22<sub>n</sub> is associated with each lock of the system, and after each impact by the step-by-step switch 21, the cam switch automatically causes the expansion cycle of the lock concerned to take place once.

Fig. 2 shows a simplified arrangement of the control system. It is used when all valves 13 to 13<sub>n</sub> are to open simultaneously. In this case, the pressure of the tube system is measured through a measuring device 17. The measured value thereof is transferred to the input of a regulator 18, which has a PI-behaviour (proportional and reset control action). This regulator directly controls operation of the cam switch 22, whereby the expansion cycle of all locks is caused to take place simultaneously.

If the initial mixing in the storage vessel 4 is carried out at a higher pressure than the pressure used in the reaction, throttle members 16, 16<sub>1</sub>, 16<sub>2</sub>, 16<sub>3</sub> to 16<sub>n</sub> for example overflow valves, can be arranged upstream of the separate tube sections, the said valves causing the reduction to the reaction pressure.

The arrangement shown in figure 2 may be modified by the provision of stirrers 23, 23<sub>1</sub>, 23<sub>2</sub> to 23<sub>n</sub> as shown in figure 3, in which the tube sections (unreferenced) are represented to be vertical.

## EXAMPLE

In accordance with United Kingdom Specification No. 843,974 and United Kingdom Specification No. 859,743, 2.5 kg of ethylene and 6.1 kg. of a solution consisting of 25% of vinyl acetate, 75% of tert.-butanol and 0.05% of  $\alpha,\alpha'$ -azodiisobutyric acid dinitrile are introduced under a pressure of 320 atm. gauge at room temperature and through a mixer-type autoclave provided with a stirrer-device and having a capacity of 16 litres into a tube system consisting of two tubes, the said tube system being in a water bath heated to 63° C. This tube system has a total volume of 100 litres and consists of two high-pressure tubes connected in parallel, the internal diameter thereof being 45 mm and the volume of each being 50 litres. Situated downstream of each tube is a chamber with valves on the input and output sides, each with a content of 220 cc., through which the solution of the polymer is intermittently extracted. The valves are open for 3 seconds and closed for 72 seconds. The pressure drop with one filling of the sluice unit is 20 atm. gauge on each occasion in the tube concerned. The product withdrawn

from the sluice is freed from gas and solvent and isolated in dry form. 1.2 kg per hour of a copolymer of uniform consistency are obtained, the copolymer containing 41% of vinyl acetate and 58.5% of ethylene. The installation can be operated without any interruption over long periods of time, while with the same mixture in an autoclave system in which the withdrawal of the product takes place continuously, the system must be shut down after a few days, since a uniform temperature control is no longer possible and deposits are formed in the autoclave. A fractionation of the product by precipitation showed a high degree of uniformity, both as regards the molecular weight and the chemical composition. The product is vulcanized for 30 minutes at 151°C. in accordance with the process disclosed in United Kingdom Patent Specification No. 853,640 and had the physical properties indicated in the Table. The values of a product which was obtained under the same conditions in an autoclave system in which the product was withdrawn continuously are given by way of comparison.

	Tube Reactor	Autoclave System
Tensile strength kg/cm <sup>2</sup>	180	130
Breaking elongation %	470	440
Shore Hardness at 20° C.	66	68
Impact Elasticity (%) at 20° C.	51	47

The tube reactor which has been described is especially suitable for continuously carrying out chemical reactions, with which viscous or non-homogeneous products are used or formed, for example for the production of compounds of high molecular weight by polymerization or polycondensation reactions, and also for the conversion of products of high molecular weight, for example by hydrogenation.

It is for example suitable for the polymerization or copolymerization of olefines or olefine derivatives, such as ethylene, propylene, isobutylene, styrene, butadiene, isoprene, vinyl acetate, vinyl propionate, isopropenyl acetate, vinyl chloride, acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid as well as their esters, amides, nitriles, and anhydrides.

With such polymerization reactions, due to the parallel connection of many tubes, a smaller pressure drop, a more closely defined residence time and thus, in many cases, a narrower molecular weight distribution, better qualities of the product and a higher degree

of polymerisation are achieved than when the tubes are arranged in series.

## WHAT WE CLAIM IS:—

1. A reactor system consisting of a number of tube sections which are connected in parallel to a common proportioning and mixing device and each of which is provided at its outlet with a lock comprising a chamber having an inlet and an outlet valve, which valves are controlled by devices so as to effect the withdrawal of substances from the individual tube sections of the reactor system in a predetermined cyclic order or simultaneously at predetermined intervals.

2. A reactor system as claimed in claim 1, wherein the valves are provided with driving means which are actuated by a time relay.

3. A reactor system as claimed in claim 1, wherein the valves are provided with driving means which are actuated by a contact manometer which is set at the required working pressure of the reactor system.

4. A reactor system as claimed in claim 1, wherein the ratio of each chamber volume to

the volume of the corresponding tube section is the same.

- 5 5. A reactor system as claimed in claim 1, wherein the tube sections are provided with stirrers.
6. A reactor system substantially as described with reference to figures 1, 2 or 3 of the accompanying drawings.

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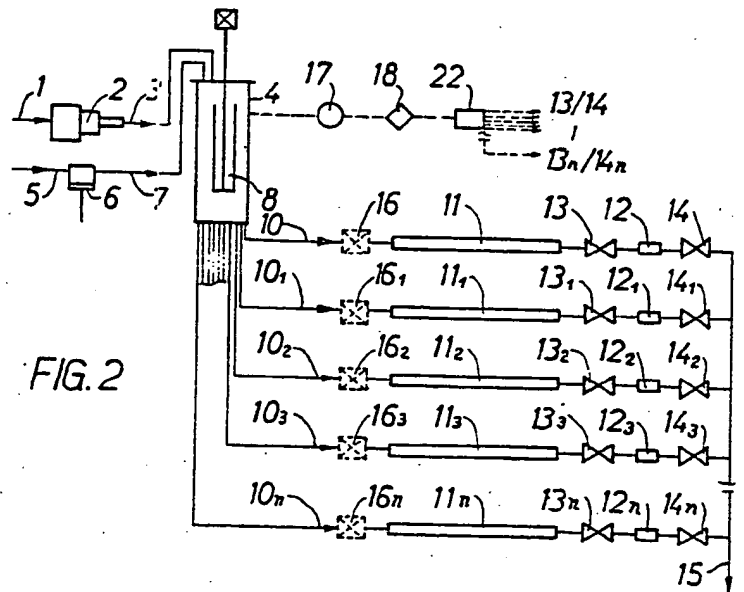
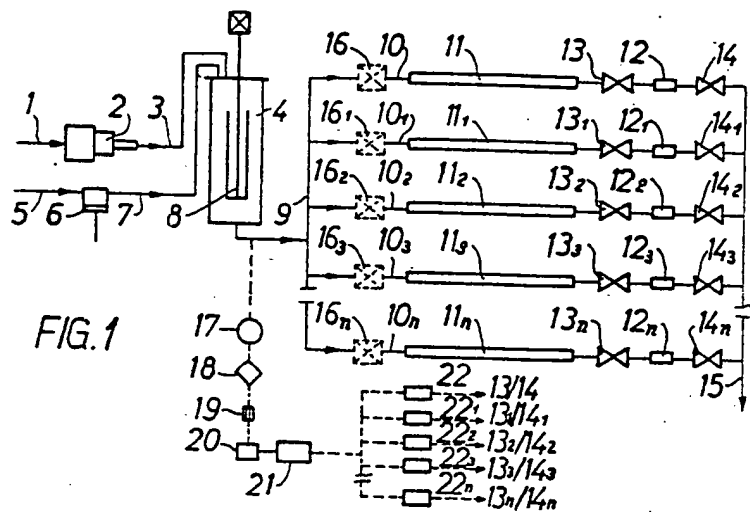
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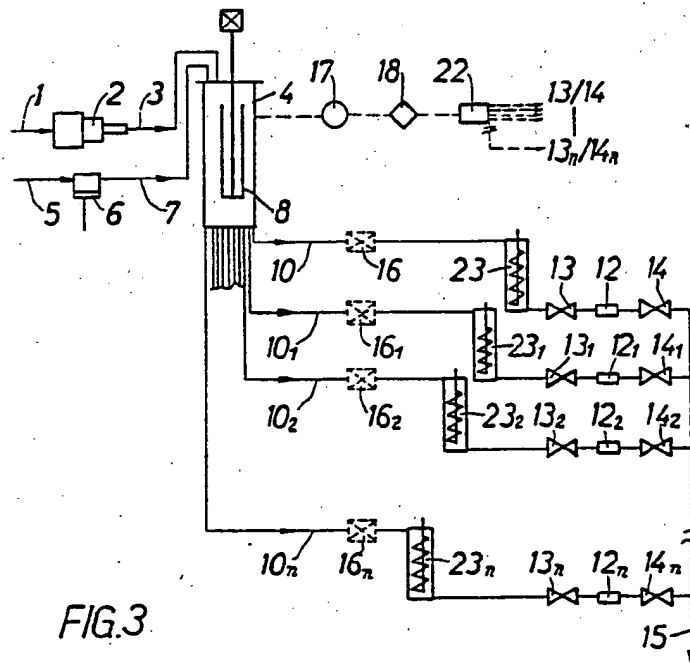
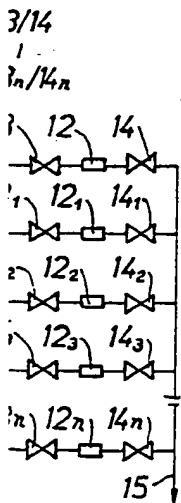
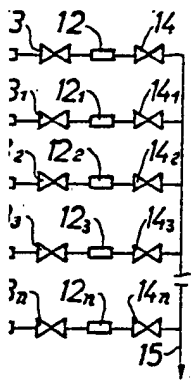
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COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of  
the Original on a reduced scale

Sheets 1 & 2



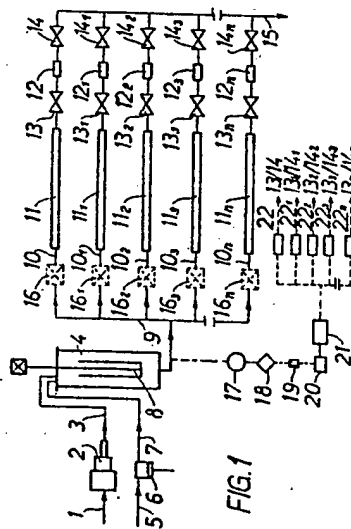


FIG. 1

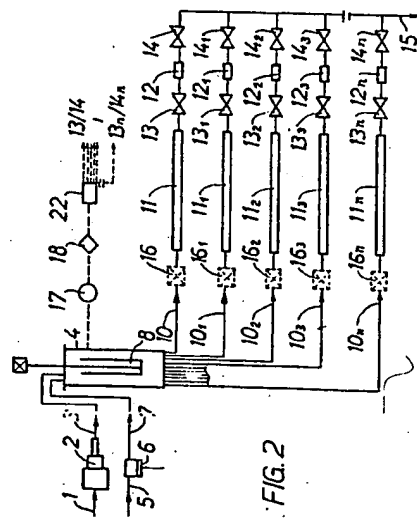


FIG. 2

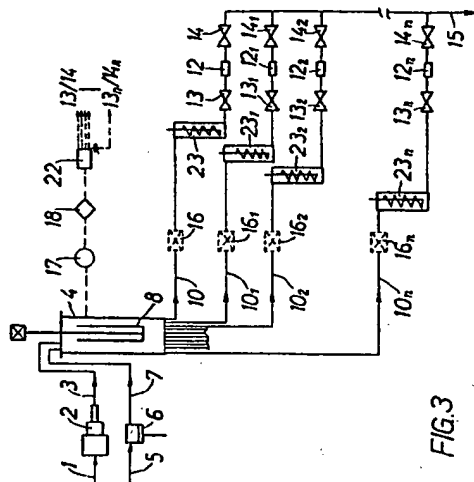


FIG. 3